

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/083829 A1(51) International Patent Classification⁷: C11D 3/395, 3/39(74) Agent: GILL JENNINGS & EVERY; Broadgate House,
7 Eldon Street, London EC2M 7LH (GB).

(21) International Application Number: PCT/GB02/01641

(22) International Filing Date: 8 April 2002 (08.04.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0109137.0 11 April 2001 (11.04.2001) GB(71) Applicant (for all designated States except US): **WARWICK INTERNATIONAL GROUP LIMITED**
[GB/GB]; Mostyn, Holywell, Flintshire CH8 9HE (GB).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HAQUE, Ekram**
[GB/GB]; C/o Warwick International Limited, Mostyn, Holywell, Flintshire CH8 9HE (GB). **SHEANE, Carol, A.** [GB/GB]; C/o Warwick International Limited, Mostyn, Holywell, Flintshire CH8 9HE (GB).

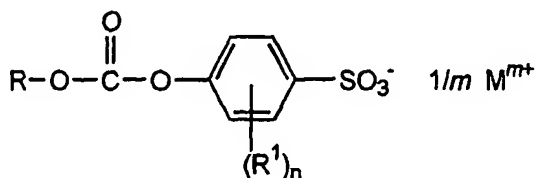
Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/083829 A1

(54) Title: MIXED BLEACH ACTIVATOR COMPOSITIONS AND METHODS OF BLEACHING

(57) Abstract: The present invention provides a bleaching composition comprising a carbonate bleach activator compound of the general structural formula (I) wherein R is selected from the group consisting of C₆₋₂₄ alkyl, C₆₋₂₄ alkyl, C₆₋₂₄ alkenyl, C₆₋₂₄ alkynyl and C₇₋₂₄ aralkyl; R¹ is a C₁₋₁₂ alkyl group, n is an integer of 0 to 4, M is a cation and m is 1 or 2; and a hydrophilic acyl organoamide bleach

activator. The present invention additionally provides a detergent composition and method of bleaching a substrate utilising the above mentioned mixture of bleach activators.

BEST AVAILABLE COPY

MIXED BLEACH ACTIVATOR COMPOSITIONS AND METHODS OF BLEACHING

Field of Invention

5 This invention relates to improved bleach activator and bleaching compositions. In particular, the invention relates to novel bleaching and detergent compositions which provide an effective overall bleaching performance on textiles and fabrics over a wide variety of stains.

Background of the Invention

 Detergent bleach compositions for washing at higher temperatures are well known in the art. As bleaching agents they normally contain a peroxide compound which liberates hydrogen peroxide in aqueous solution, such as the peroxyhydrates, including alkali metal perborates,
15 percarbonates, perphosphates and persilicates, urea peroxide and the like. These bleaching agents are only effective at higher temperatures of the bleaching solution, i.e. from 80°C up to the boil.

 It is known that the bleach activity of peroxide bleach compounds can be improved so as to become effective at lower wash temperatures, e.g. 40-
20 60°C, by the use of peroxyacid precursors, often also referred to as bleach activators.

 Numerous substances have been disclosed in the art as effective bleach activators.

 GB patent 855,735, which discloses the broad class of "acyl
25 organoamides", to which the currently most widely used N,N,N'-tetraacetyl ethylene diamine (TAED) belongs.

 Typically, the substances that have been proposed and utilised as bleach activators are organic compounds which react with the perhydroxide anion (OOH⁻) of the hydrogen peroxide yielded by the peroxide bleach in the
30 bleaching solution, to form a peroxyacid which is more reactive than the peroxide bleach alone, to effect bleaching at bleach solution temperatures of

below 60°C. A particular type of stain which is effectively removed by one specific peroxyacid precursor-hydrogen peroxide combination, may not be as effectively removed by another peroxyacid precursor/H₂O₂ system. Since many classes of soiling are encountered in household and industrial practice, there is not one single bleach activator which is effective on all sorts of bleachable soiling and stains. Domestic soils contain hydrophilic and hydrophobic components.

Various attempts have been made to improve the overall bleaching performance on fabrics over a wide range of stains and soilings by bleach system combinations, but such attempts have in general met with only limited success and/or specific drawbacks.

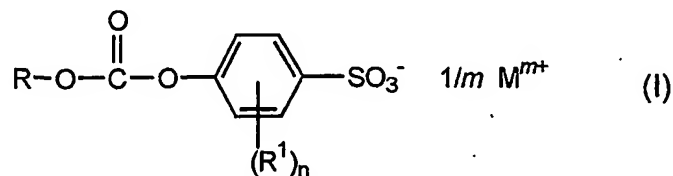
A continuing trend towards even lower wash temperatures has furthermore presented a constant need for peroxide bleaches with real efficacy at temperatures of 40°C and therebelow.

EP-A-0257700 (Unilever) discloses the use of a bleach system comprising a percompound and a mixture of TAED and sodium nonanoyloxy benzene sulphonate.

EP-A-0202698 discloses a novel p-sulphophenyl alkyl carbonate, having an alkyl group containing 6 to 10 carbon atoms. Detergent compositions containing this type of activator are disclosed.

Summary of Invention

The present invention provides a bleaching composition comprising a carbonate bleach activator compound of the general structural formula (I)



wherein R is selected from the group consisting of C₆₋₂₄ alkyl, C₆₋₂₄ alkenyl, C₆₋₂₄ alkynyl and C₇₋₂₄ aralkyl; R¹ is a C₁₋₁₂ alkyl group, n is an integer of 0 to 4, M is a cation and m is 1 or 2;

and a hydrophilic acyl organoamide bleach activator.

The present invention additionally provides a detergent composition and a method of bleaching a substrate utilising the above mentioned mixture of bleach activators.

5

Detailed Description of the Invention

In compound (I), group R is preferably a C₆₋₁₂, more preferably C₆₋₁₀, most preferably C₈ alkyl group. R may be branched or linear, preferably linear. Where R is branched, R is preferably 2-ethylhexyl. In any aralkyl
10 group R the aryl part may be substituted, for instance by C₁₋₁₈ alkyl, preferably C₆₋₁₂ alkyl, but is preferably unsubstituted.

R¹ is preferably a C₁₋₆ alkyl group, most preferably a methyl or ethyl group.

n is preferably an integer of 0 or 1, most preferably 0.

15 M is selected from the group consisting of alkali metals, alkaline earth metals and ammonium groups, more preferably alkali metals, most preferably sodium.

Preferred compounds of formula (I) are sodium or potassium p-(sulphophenyl *n*-octyl) carbonate, sodium or potassium p-(sulphophenyl *n*-
20 nonyl) carbonate, and sodium or potassium p-(sulphophenyl *n*-decyl) carbonate.

Most preferably, compound (I) is sodium p- (sulphophenyl *n*-octyl) carbonate.

The hydrophilic acyl organoamide is an amide derived from an
25 organic carboxylic acid and an organic group substituted amine compound containing at least one acyl group attached to the nitrogen atom.

By hydrophilic acyl organoamide is meant that it is the peracid of the acyl group which is hydrophilic.

30 Examples of peroxyacid precursor compounds falling under this group are:

(a) N,N-diacetylaniline and N-acetylphthalimide;

(b) N-acylhydantoins, such as N,N'-diacetyl-5,5-dimethylhydantoin;

(c) Polyacylated alkylene diamines, such as N,N,N',N'-tetraacetyl ethylene diamine (TAED) and N,N,N',N'-tetraacetyl methylene diamine (TAMD) as disclosed in British Patent No. 907,356;

(d) Acylated glycolurils, such as tetraacetyl glycoluril (TAGU) as disclosed in British Patent No. 1,246,338;

(e) alpha-Acyloxy-(N,N')-polyacyl malonamides, such as alpha-acetoxy-(N,N')diacetyl malonamide as disclosed in U.S. Patent No. 3,183,266.

The acyl organoamide generally has the structural formula
 $R^2CONR^3R^4$, in which R^2 is selected from C_{1-12} alkyl, C_{2-12} alkenyl and C_{2-12} alkynyl groups, R^3 is a second acyl radical and R^4 is selected from C_{1-12} alkyl, C_{2-12} alkenyl and C_{2-12} alkynyl groups, any of which may be substituted with one or more mono-or di- acyl amino groups.

Preferably, the acyl organoamide comprises two amide groups linked through an alkanediyl group.

In a particularly preferred embodiment, the acyl organoamide has the structural formula (II)



wherein R^5 is a C_{1-6} alkanediyl group, preferably an ethanediyl group, and each R^6 is individually selected from a C_{1-6} alkyl group, preferably methyl, ethyl or propyl. Preferably all R^6 are the same.

Most preferably, the acyl organoamide is N,N,N',N'-tetracetylene diamine (TAED).

The above mentioned compounds are advantageously incorporated into a detergent composition which, in addition to the bleach activators, contains a bleaching agent, which under alkaline conditions generates hydrogen peroxide.

Examples of suitable, commonly used bleaching agents include alkali metal percarbonate, perborate, persilicate, perphosphate, persulphate and

perpyrophosphate, herein after "percompounds". A preferred bleaching agent is sodium percarbonate.

The bleaching agent can be present in the detergent composition in amounts of from 5-99% by weight. The detergent composition of the invention may consist solely of a percompound and the bleach activator mixture when used as a pure bleach product or as a bleach additive to detergent compositions. In that case the composition will comprise from 50-99% percompound and from 50-1% of the bleach activators, and optional diluents.

Generally, compound (I) is present in a detergent composition in an amount of 0.1 to 50% by weight, preferably 0.5 to 10% by weight, most preferably 1 to 2% by weight.

Generally, the organoamide is present in a detergent composition in an amount of 0.1 to 50% by weight, preferably 0.5 to 10% by weight, most preferably 3 to 5% by weight.

Preferably the detergent composition will contain at least one surface-active agent selected from the group consisting of soaps, synthetic anionic, nonionic, cationic, amphoteric and zwitterionic surfactants and mixtures thereof, in an amount of from about 2 to 40% by weight of the composition.

Generally, mixtures of the above surface-active agents are used; mixtures of synthetic anionic, synthetic nonionic surfactants and soap are commonly used.

Suitable anionic surfactants are alkali metal soaps of fatty acids, fatty acid-protein condensation products, primary or secondary alkyl sulphates, fatty-acid alkanolamide sulphates, sulphated alkyl- or alkylphenol-polyglycolethers, fatty acid isethionates, fatty acid taurides, alkylbenzene sulphonates, alkane sulphonates, olefin sulphonates, salts of alpha-sulpho fatty acids and esters thereof, and other known surface-active compounds of the sulphate and sulphonate type.

Suitable examples of nonionic surfactants are alkyl and acyl polyglycolethers, alkylphenol polyglycolether, fatty acid alkanolamides and

their ethoxylated products, ethoxylated polypropylene glycolethers, amine oxides and fatty acid sugar esters.

The bleach activators according to the present invention commonly are presented in a detergent matrix. Alternatively, the bleach activators according to the invention may be used *per se* in a detergent composition. Usually the total amount of detergency matrix in a detergent composition of the invention will be from about 5% to about 70% by weight of the detergent composition.

Examples of known detergent matrices are based on sodium tripolyphosphate, sodium orthophosphate, sodium pyrophosphate, sodium trimetaphosphate, sodium ethane-1-hydroxy-1,1-diphosphonate, sodium carbonate, sodium silicate, sodium citrate, sodium oxydiacetate, sodium nitrilotriacetate, sodium ethylenediaminetetraacetate, sodium salts of long-chain dicarboxylic acids, for instance straight-chain (C_{10} to C_{20}) succinic acids and malonic acids, sodium salts of alpha-sulphonated long-chain monocarboxylic acids, sodium salts of polycarboxylic acids, i.e. acids derived from the polymerization or copolymerization of unsaturated carboxylic acids and unsaturated carboxy acid anhydrides such as maleic acid, acrylic acid, itaconic acid, methacrylic acid, crotonic acid and aconitic acid, and the anhydrides of these acids, and also from the copolymerization of the above acids and anhydrides with minor amounts of other monomers, such as vinyl chloride, vinyl acetate, methyl methacrylate, methyl acrylate and styrene, polyacetal carboxylates, and, modified starches such as starches oxidized, for example, using sodium hypochlorite, in which some anhydroglucose units have been opened to give dicarboxyl units.

Another type of detergent matrix which can be used, either alone or in admixture in the detergent composition with other materials useful as builders, is a cation-exchange material, especially a sodium aluminosilicate such as described in GB Patent No. 1,429,143 or in Netherlands Patent Application No. 7403381.

Preferred materials of this type have the formula:

(Na_2O)_{0.7-1.1}· $\text{Al}_2\text{O}_3(\text{SiO}_2)$ _{1.3-3.3} and may be amorphous or crystalline, with some bound water usually in an amount of about 10-30% depending on the drying conditions used. Such water-insoluble aluminosilicate cation-exchange materials are available as very finely divided powder, commercially known under various grades of zeolites, e.g. Zeolite A and Zeolite B.

Furthermore, any other non-interfering ingredients normally used in detergent compositions in minor amounts, which serve to improve the bleaching and laundering characteristics of the composition or which add aesthetic appeal to the composition, may also be incorporated.

One such important minor ingredient serving to improve the bleaching and laundering characteristics is a peroxide stabilising agent usually a heavy metal sequestrant such as ethylene diamine tetra(methylene phosphonic acid) or its alkali metal salts as disclosed in GB Patent No. 1,392,284, and other selected types of compounds as disclosed in GB Patent No. 2,033,937.

Other minor ingredients can include washing alkalis and buffering agents, sequestering agents such as EDTA, polymeric co-builders, suds-controlling agents, soil-suspending agents and anti-redeposition agents, enzymes, particularly proteolytic enzymes, corrosion inhibitors, optical brighteners, colouring agents, heavy metal catalysts, perfumes, bacteriostats and filler materials.

Generally, such minor components comprise no more than about 20% by weight of the bleach composition.

The detergent composition according to the invention may be in a form-varying from powdered to granular and may be prepared by methods known in the art, such as crystallisation or spray drying of an aqueous slurry or mechanical mixing of the substances.

The invention is not confined to solid detergent compositions but also comprises liquid detergent compositions containing the present bleaching activators.

The present bleaching activators may also be added separately, in the form of a detergent additive containing the bleach activators, to aqueous wash liquor containing at least a surfactant and a hydrogen peroxide generating bleaching agent. To this end the bleach activators may be
5 applied in the form of powder, granule preferably provided in a matrix, such as described above or in the form of a solution or dispersion. The bleaching activator may also be used in the form of a coated particle. Examples of suitable coating materials are ethoxylated fatty acids and poly(ethylene oxide).

10 The present invention also includes methods of bleaching fabrics and textiles in which the bleach composition and a bleaching agent are dissolved into the water to form a detergent liquor, which is then contacted with the fabric or textiles.

The present invention has particular utility in the fields of laundry and
15 textile bleaching and cleaning. In particular, the invention has been shown to be particularly effective in the bleaching and cleaning of laundry and textiles comprising both hydrophilic and hydrophobic stains. This is due to the hydrophobic nature of the carbonate bleach activator and the hydrophilic nature of the acyl organoamide.

20 The present invention will now be described with reference to the examples.

Example 1

A 4% TAED/1% SC905 (sodium-4-(sulphophenyl octyl) carbonate) mixed
25 system was tested to investigate wash benefits are obtained at 40°C under European conditions (8 g/l concentration of wash components).

A blank formulation containing WMP base detergent formulation and sodium percarbonate PCS was carried out. The % stain removal results of this wash were deducted from that of the mixed activator systems and also from
30 those of the individual components. These results were used to assess the actual benefits seen from each formulation.

Washes were carried out using a Miele domestic laundry washing machine at 40°C, using the short wash, cotton cycle. Details of swatches used follows the tables. Graphical results can be found in Figures 1, 2 and 3.

5 Formulation Details

Formulation	WMP Base (g)	PCS (g)	TAED (g)	SC905 (g)	SNOBS (g)
F1.1	68	9.5637	-	-	-
F1.2	68	9.5637	3.2	0.8097	-
F1.3	68	9.5637	3.2	-	-
F1.4	68	9.5637	-	0.8097	-
F1.5	68	9.5637	-	0.8097	3.4745
F1.6	68	9.5637	-	-	3.4745

Comparison of mixed systems to the sum of individual components.

SWATCHES	4%TAED/1% SC905 (F1.2)	Sum of individual components (F1.3/F1.4)	4% SNOBS/ 1% SC905 (F1.5)	Sum of individual components (F1.4/F1.6)
RW	14.2	13.8	5.2	9.8
BC2	8.0	4.6	9.0	8.5
BC3	11.5	5.2	5.2	2.3
BC4	3.8	1.3	3.8	6.6
BC5	3.2	0.5	1.2	-2.2
CS10	1.3	4.5	4.1	9.5
CS15	17.8	12.0	5.9	11.7
CS5S	0.0	-0.6	-0.1	1.2
CS9	-0.7	-0.6	1.0	0.9
AS4	3.3	2.1	10.0	10.9
AS9	0.6	0.0	5.0	4.8
AS12	-2.4	-2.4	4.3	3.2
E101	1.7	-5.7	-0.1	-3.3
E116	-22.3	-19.9	-14.4	-18.1
WFK10C	-2.0	-3.4	-1.0	-0.2
WFK10P	1.8	-2.3	9.5	8.3

Stain removal results as %Z Brightness

SWATCHES	Formulation					
	Base plus	4%TAED/ 1%SC905	4% TAED	1% SC905	4%SNOBS/ 1% SC905	4% SNOBS
	PCS (F1.1)	(F1.2)	(F1.3)	(F1.4)	(F1.5)	(F1.6)
RED WINE	34.0	48.2	44.4	37.4	39.2	40.4
BC2	5.9	13.9	9.1	7.3	14.9	13.0
BC3	8.6	20.1	15.2	7.2	13.8	12.3
BC4	14.0	17.8	13.8	15.5	17.8	19.1
BC5	41.6	44.8	43.4	40.3	42.8	40.7
CS10	35.1	36.4	36.9	37.8	39.2	41.9
CS15	27.7	45.5	35.1	32.3	33.6	34.8
CS5S	19.1	19.1	17.9	19.7	19.0	19.7
CS9	68.8	68.1	68.5	68.5	69.8	70.0
AS4	8.3	11.6	8.4	10.3	18.3	17.2
AS9	49.0	49.6	48.8	49.2	54.0	53.6
AS12	49.5	47.1	48.5	48.1	53.8	54.1
E101	28.1	29.8	22.9	27.6	28.0	25.3
E116	45.1	22.8	29.6	40.7	30.7	31.4
WFK10C	30.0	28.0	26.4	30.2	29.0	29.6
WFK10P	60.9	62.7	59.4	60.1	70.4	70.0

Swatch details

Bleachable Stains:

CS15 - tomato

Detergency Responsive Stains:

AS9 - pigment / oil (<60°C)

AS12 - an overall performance monitor for all temperatures. Has a low concentration of milkpowder and therefore also has a small (proteolytic) enzyme response. AS12 also responds to builder/water hardness, oxidising bleaches (slightly), wash time and product concentration.

E101 - olive oil / carbon black stains.

E116 - blood / milk / carbon black stains. Fixing of this stain can, in some circumstances, be used as a measure of bleach performance.

WFK10C - soiled cotton, WFK soil

WFK10P - red pepper

Stain removal was assessed by %Z Brightness using the Spectraflash 500.

The results of the 4% TAED/1% SC905 mixed system confirmed the complimentary effects seen during evaluations. This will be due to the presence of hydrophilic (TAED) and hydrophobic (SC905) activators, which will work over a wide range of stains. The mixed system also showed improved overall performance over the sum of the individual components.

The 4% SNOBS/1% SC905 mixed system did not show any overall complementary effects.

Example 2

Following on from the evaluation of mixed activator systems under European conditions for patent data, tests of SC905 (sodium-4-(sulphophenyl octyl) carbonate) plus TAED under Asia Pacific conditions were carried out. The testing was carried out using two different levels of activator, 2.5%/2.5% and 4%/1% TAED/SC905 to ensure that a full performance profile was completed.

A blank formulation containing Maxkleen 9 base detergent formulation and sodium percarbonate (PCS) was tested and used as the baseline stain removal to determine whether any improvements were seen.

Washes were carried out using a Japanese domestic laundry washing machine at 30°C, using the soak normal cycle, medium fill. Details of swatches used follows the tables. Graphical results can be found in Figures 4, 5, 6 and 7.

Formulation Details

Formulation	Maxkleen (g)	PCS (g)	TAED (g)	SC905 (g)
Action Plan 3 - 4% TAED/1% SC905				
F3.1	52.28	7.3023	-	-
F3.2	52.28	7.3023	2.46	0.6225
F3.3	52.28	7.3023	2.46	-
F3.4	52.28	7.3023	-	0.6225
Action Plan 4 - 2.5% TAED/5% SC905				
F4.1	52.28	7.3023	-	-
F4.2	52.28	7.3023	1.5375	1.5562
F4.3	52.28	7.3023	1.5375	-
F4.4	52.28	7.3023	-	1.5562

Action Plan 3 Washes - Stain Removal as % Z Brightness

SWATCHES	Formulation			
	Base & PCS	4% TAED/ 1%SC905	4% TAED	1% SC905
	(F3.1)	(F3.2)	(F3.3)	(F3.4)
RW	30.7	35.4	34.5	32.5
BC2	3.6	6.2	4.8	3.8
BC3	2.3	5.6	4.5	3.0
BC4	11.6	14.4	12.8	12.4
BC5	29.8	32.8	31.8	32.1
CS10	33.0	32.4	28.7	34.9
CS11	17.7	21.5	21.3	18.2
CS14	38.9	42.5	41.6	39.3
CS15	29.2	32.1	31.8	31.9
CS5S	18.3	17.7	17.3	18.6
CS9	66.5	67.7	66.8	67.2
AS4	6.9	8.7	6.2	7.3
AS9	53.4	53.0	49.7	49.2
AS12	45.1	44.6	44.4	45.7
E101	22.7	26.9	24.3	25.8
E116	25.0	15.4	18.7	21.6
WFK10C	29.8	25.3	29.5	31.4
WFK10P	57.5	58.5	57.9	59.6

Difference in Stain Removal Compared to Base & PCS Formulation

SWATCHES	Formulation	
	4% TAED/1%SC905 (F3.2)	Sum of Individual Components (F3.3/F3.4)
RED WINE	4.7	5.6
BC2	2.6	1.4
BC3	3.3	2.9
BC4	2.8	2.0
BC5	3.0	4.3
CS10	-0.6	-2.4
CS11	3.8	4.1
CS14	3.6	3.1
CS15	2.9	5.3
CS5S	-0.6	-0.7
CS9	1.2	1.0
AS4	1.8	-0.3
AS9	-0.4	-7.9
AS12	-0.5	-0.1
E101	4.2	4.7
E116	-9.6	-9.7
WFK10C	-4.5	1.3
WFK10P	1.0	2.5

Action plan 4 Washes - Stain Removal as % Z Brightness

SWATCHES	Formulation			
	Base & PCS (F4.1)	2.5% TAED/ 2.5% SC905 (F4.2)	2.5% TAED (F4.3)	2.5% SC905 (F4.4)
RW	33.1	37.5	33.5	35.5
BC2	4.3	10.3	5.0	7.5
BC3	2.4	8.8	3.2	5.7
BC4	12.4	15.1	12.9	14.7
BC5	18.4	22.7	16.4	18.0
CS10	33.8	38.6	34.2	39.4
CS11	18.8	21.4	19.1	19.9
CS14	41.4	45.4	41.0	43.0
CS15	33.3	36.2	32.5	32.8
CS5S	18.4	18.3	18.0	19.7
CS9	67.1	68.1	67.3	68.6
AS4	7.1	11.6	6.8	10.8
AS9	52.4	53.4	52.0	53.3
AS12	44.4	46.4	47.6	48.2
E101	28.4	30.2	27.2	29.2
E116	24.1	13.3	19.6	16.5
WFK10C	35.6	36.3	32.1	30.0
WFK10P	59.1	62.3	58.8	61.7

Difference in Stain Removal Compared to Base & PCS Formulation

SWATCHES	Formulation	
	2.5% TAED/ 2.5%SC905	Sum of Individual Components
RED WINE	4.4	2.8
BC2	6.0	3.9
BC3	6.4	4.1
BC4	2.7	2.8
BC5	4.3	-2.4
CS10	4.8	6.0
CS11	2.6	1.4
CS14	4.0	1.2
CS15	2.9	-1.3
CS5S	-0.1	0.9
CS9	1.0	1.7
AS4	4.5	3.4
AS9	1.0	0.5
AS12	2.0	7.0
E101	1.8	-0.4
E116	-10.8	-12.1
WFK10C	0.7	-9.1
WFK10P	3.2	2.3

Swatch details - as Example 1, plus

Bleachable Stains:

CS11 Redcurrant Juice

CS14 Morello Juice

CS15 Bilberry Juice

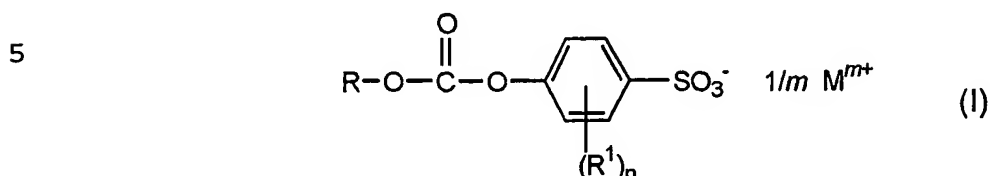
The results of the 2.5% TAED/2.5% SC905 mixed system confirmed the improvement in bleachable stain removal, compared to the sum of the individual activators as seen during the European evaluation.

The 4% TAED/1% SC905 mixed system did not show any overall complimentary effects, although there was a slight improvement in stain removal when compared to TAED alone. This was the ratio of SC905 and TAED which showed benefits under European conditions (Example 1).

In conclusion, the mixed activator system consisting of 2.5% SC905 plus 2.5% TAED showed improved stain removal under Asia Pacific conditions compared with the sum of the individual activators.

Claims

1. A bleaching composition comprising a bleach activator compound of the general structural formula (I)



10 wherein R is selected from the group consisting of C₆₋₂₄ alkyl, C₆₋₂₄ alkenyl, C₆₋₂₄ alkynyl and C₇₋₂₄ aralkyl; R¹ is a C₁₋₁₂ alkyl group, n is an integer of 0 to 4; M is a cation and m is 1 or 2;

and a hydrophilic acyl organoamide bleach activator.

2. A bleaching composition according to claim 1, wherein group R is a C₆₋₁₂, more preferably C₆₋₁₀, most preferably C₈ alkyl group.

15 3. A bleaching composition according to claim 1 or 2, wherein R is linear.

4. A bleaching composition according to claims 1, 2 or 3, wherein R¹ is a C₁₋₆ alkyl group, most preferably a methyl or ethyl group.

20 5. A bleaching composition according to any preceding claim, wherein n is an integer of 0 or 1, preferably 0.

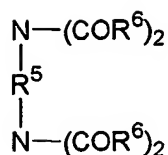
6. A bleaching composition according to any preceding claim, wherein M⁺ is sodium or potassium, preferably sodium.

7. A bleaching composition according to any preceding claim, wherein compound (I) is sodium p-(sulphophenyl ⁿoctyl) carbonate.

25 8. A bleaching composition according to any preceding claim, wherein the hydrophilic acyl organoamide has the structural formula R²CONR³R⁴, in which R² is selected from C₁₋₁₂ alkyl, C₂₋₁₂ alkenyl and C₂₋₁₂ alkynyl groups, R³ is a second acyl radical and R⁴ is selected from C₁₋₁₂ alkyl, C₂₋₁₂ alkenyl and C₂₋₁₂ alkynyl groups, any of which may be substituted with one or more acyl organoamide groups.

30

9. A bleaching composition according to claim 8, wherein the hydrophilic acyl organoamide has the structural formula (II)



5 wherein R^5 is a C_{1-6} alkanediyl group, preferably an ethanediyl group, and each R^6 is individually selected from a C_{1-6} alkyl group, preferably methyl, ethyl or propyl.

10. A bleaching composition according to claim 8 or 9, wherein the hydrophilic acyl organoamide is N, N, N', N'-tetracetyl ethylenediamine.

10 11. A detergent composition comprising a bleaching composition as defined in any preceding claim and a bleaching agent.

12. A detergent composition according to claim 11, wherein the bleaching agent is selected from alkali metal percarbonate, perborate, persilicate, persulphate, perphosphate and perpyrophosphate preferably
15 sodium parcarbonate.

13. A detergent composition according to claim 11 or 12, additionally comprising a surfactant.

14. A detergent composition according to any of claims 11 to 13, wherein the surfactant is selected from the group consisting of soap, synthetic
20 anionic, nonionic, cationic, amphoteric and zwitterionic surfactants and mixtures thereof, in an amount of from about 2 to 40% by weight of the composition.

15. A detergent composition according to any of claims 11 to 14, wherein mixtures of surfactants are used.

16. A detergent composition according to any of claims 11 to 15,
25 additionally comprising a detergency builder.

17. A method of bleaching laundry or textiles in which a bleach composition according to any of claims 1 to 10 and a bleaching agent are dissolved into water to form an aqueous detergent liquor and the liquor is then contacted with the laundry or textiles.

30 18. A method according to claim 17, additionally comprising the addition of a surfactant to the wash liquor, the surfactant optionally being

presented in the same composition as the bleach activators and/or the bleaching agent.

19. A method according to claim 17 or 18, wherein the laundry/textiles have hydrophilic and hydrophobic stains.

1/4

Figure 1

% Improvement in stain removal compared to base/PCS formulation. Comparison of mixed systems to the sum of individual components

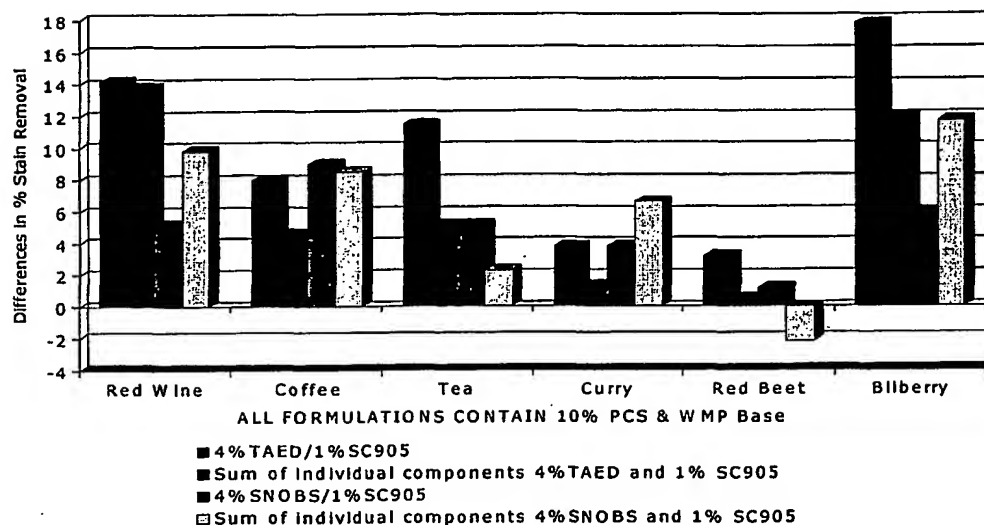
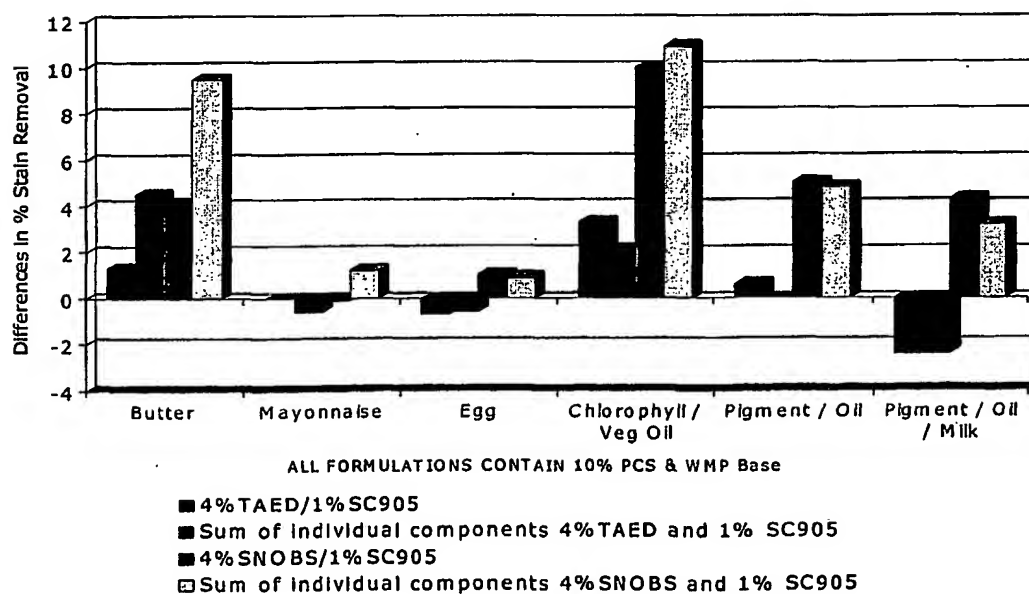


Figure 2

% Improvement in stain removal compared to base/PCS formulation. Comparison of mixed systems to the sum of individual components



2/4

Figure 3

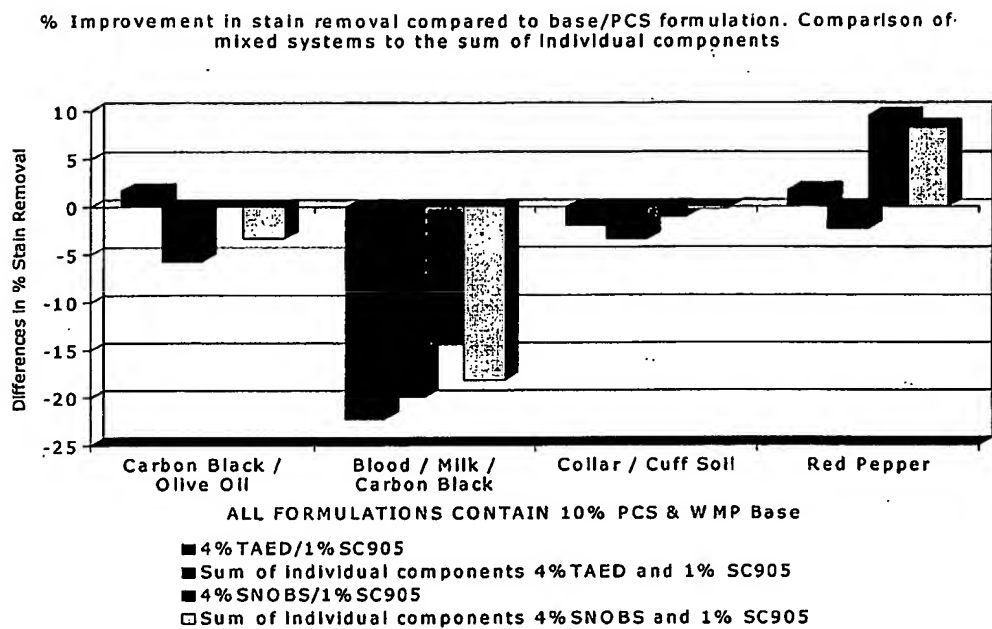
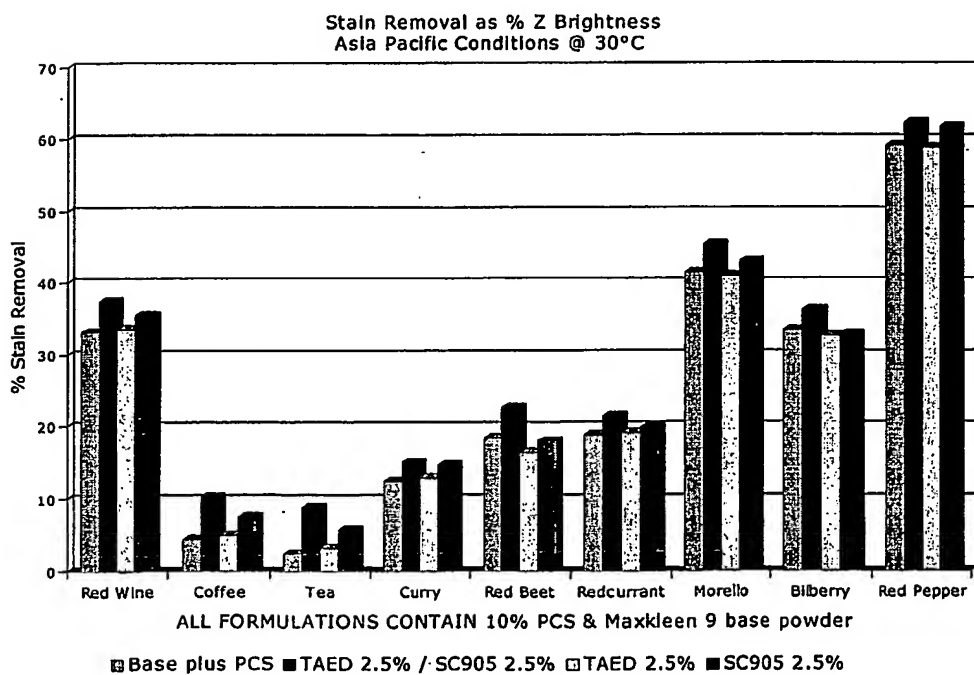


Figure 4



3/4
Figure 5

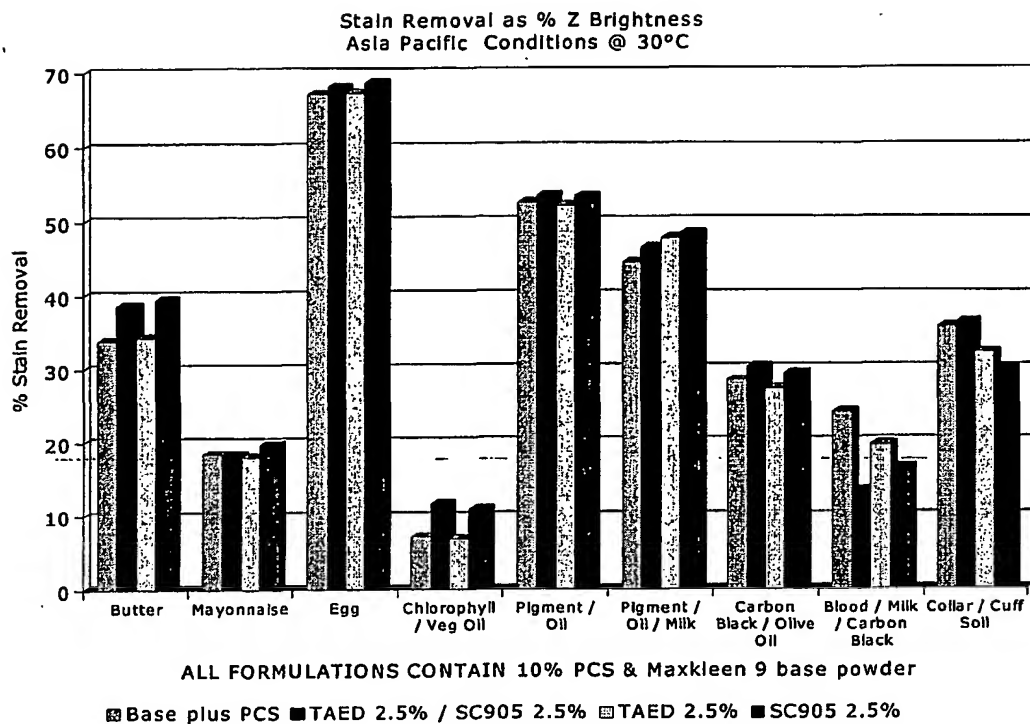
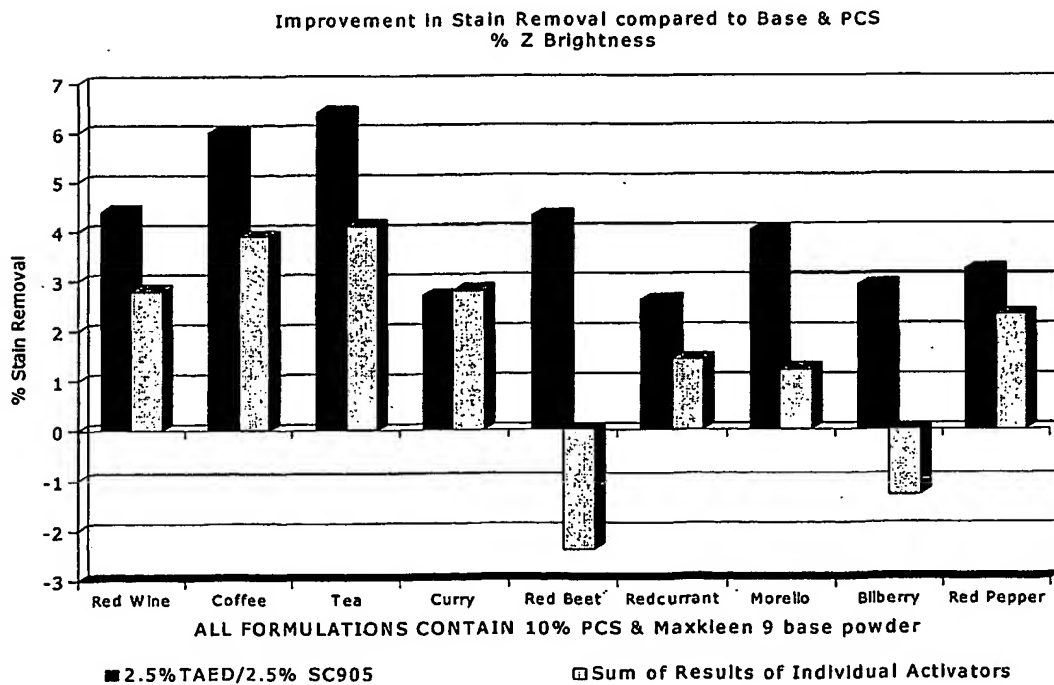
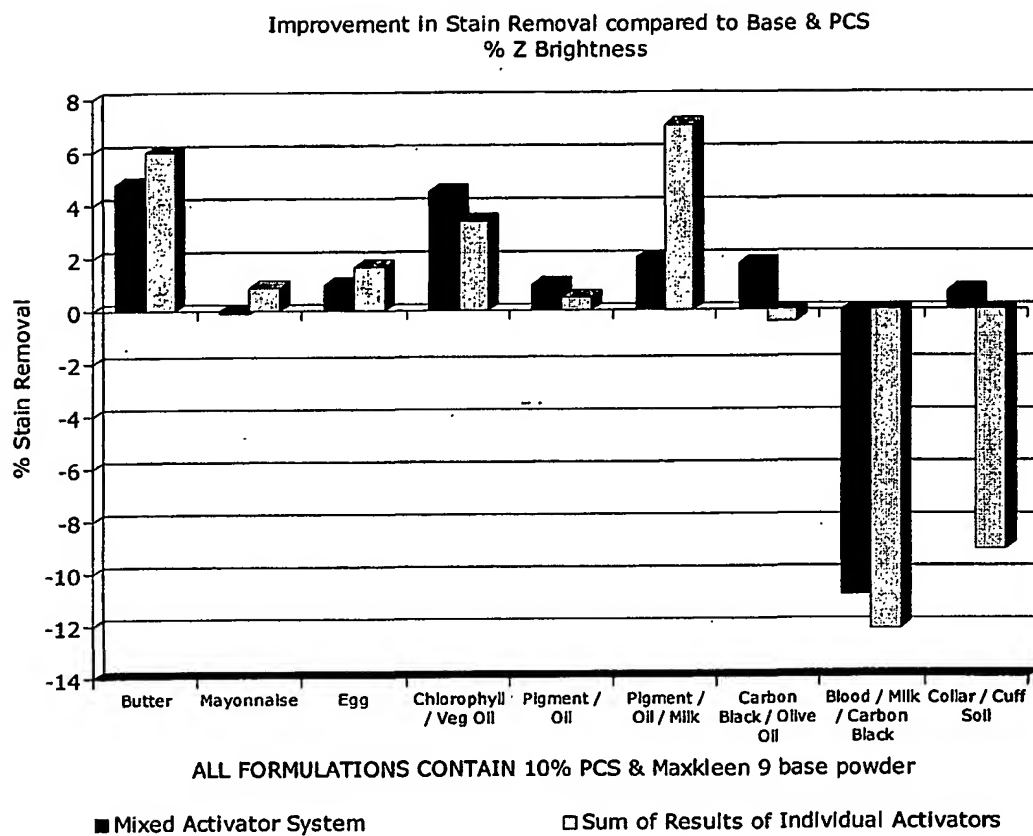


Figure 6



4/4

Figure 7



INTERNATIONAL SEARCH REPORT

Inter Application No
PC. 02/01641

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/395 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 202 698 A (AKZO NV) 26 November 1986 (1986-11-26) cited in the application claims 1-5 ---	1
A	US 5 175 333 A (JURELLER SHARON M ET AL) 29 December 1992 (1992-12-29) claims 1-14 ---	1
A	EP 0 333 248 A (UNILEVER PLC ;UNILEVER NV (NL)) 20 September 1989 (1989-09-20) claims 1-6 ---	1
A	US 5 705 091 A (STEICHEN DALE S ET AL) 6 January 1998 (1998-01-06) claims 1-4 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

9 July 2002

Date of mailing of the international search report

17/07/2002

Name and mailing address of the ISA
European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

Inter- Application No

PC  02/01641

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 402 339 A (MONSANTO CO) 12 December 1990 (1990-12-12) page 3, line 15 - line 47 ---	1
A	US 4 686 061 A (OVERKAMP JOHANNES W A ET AL) 11 August 1987 (1987-08-11) claims 1-4 -----	1

INTERNATIONAL SEARCH REPORT

International Application No

PC 02/01641

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0202698	A	26-11-1986	AT 47590 T CA 1265155 A1 DE 3666585 D1 DK 208186 A EP 0202698 A1 JP 1993608 C JP 7020920 B JP 61254549 A US 5043089 A	15-11-1989 30-01-1990 30-11-1989 08-11-1986 26-11-1986 22-11-1995 08-03-1995 12-11-1986 27-08-1991
US 5175333	A	29-12-1992	CA 2051049 A1 EP 0475513 A1 JP 6016602 A	15-03-1992 18-03-1992 25-01-1994
EP 0333248	A	20-09-1989	AU 3132689 A BR 8901203 A EP 0333248 A2 JP 2004765 A JP 6002724 B NO 891083 A ,B, ZA 8902051 A AU 614350 B2 AU 3259989 A BR 8901766 A DE 68919506 D1 EP 0337274 A2 JP 1306498 A NO 891502 A ,B, TR 23958 A	21-09-1989 31-10-1989 20-09-1989 09-01-1990 12-01-1994 18-09-1989 28-11-1990 29-08-1991 19-10-1989 28-11-1989 12-01-1995 18-10-1989 11-12-1989 16-10-1989 11-01-1991
US 5705091	A	06-01-1998	NONE	
EP 0402339	A	12-12-1990	US 5252770 A AT 112553 T CA 2018218 A1 DE 69013061 D1 DK 402339 T3 EP 0402339 A1 ES 2019851 T3	12-10-1993 15-10-1994 05-12-1990 10-11-1994 31-10-1994 12-12-1990 01-12-1994
US 4686061	A	11-08-1987	AT 53013 T CA 1261866 A1 DE 3671438 D1 DK 313186 A EP 0210674 A2 JP 2097910 C JP 7059548 B JP 62010056 A	15-06-1990 26-09-1989 28-06-1990 04-01-1987 04-02-1987 02-10-1996 28-06-1995 19-01-1987

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.